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# Phonon-assisted exciton formation and relaxation in GaAs/$Al_xGa_{1-x}As$ quantum wells

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A microscopic analysis of exciton formation and relaxation in photoexcited quantum wells is presented. The theoretical approach is based on a Monte Carlo simulation of the coupled free-carrier and exciton dynamics, and includes various mechanisms contributing to exciton formation and relaxation. Our investigation clarifies the origin of excitonic luminescence in time-resolved experiments. In particular, we address the problem of the relative efficiencies of exciton formation assisted by either LO phonons or acoustic phonons, respectively. [S0163-1829(97)51124-6]

Ultrafast optical excitation of semiconductors at energies high above the band gap is followed by a rapid relaxation of the initial nonequilibrium electron ($e$) and hole ($h$) distributions induced by various interaction mechanisms on different time scales. Parallel to this scattering dynamics, $e$-$h$ pairs may bind into excitons, which can then decay radiatively. Time-resolved optical spectroscopy[1] has provided invaluable information on the microscopic dynamics governing this coupled free-carrier vs exciton dynamics in photoexcited semiconductors. In particular, the intrinsic process of exciton formation in quantum wells (QW's) has been the subject of several experimental studies.[2–7] In spite of the broad experimental activity in this field, the scenario is not completely understood, and the dominant mechanisms responsible for exciton formation and decay are still unclear. From a detailed analysis of the variation of the excitonic line shape in time-resolved experiments, Damen *et al.*[2] found that bound-state excitons are formed with a time constant $\tau_f < 20$ ps. Since the luminescence signal was found to be nearly independent of the excess energy of the exciting laser over the gap, $E_{\rm exc} = E_{\rm las} - E_g$, they concluded that excitons are mainly created in large wave-vector states via emission of acoustic (AC) phonons, and subsequently relax to optically active states within the homogeneous linewidth.[8] Conversely, from similar experiments on thin QW's, Blom *et al.*[5] reported an oscillatory variation of the luminescence rise time $\tau_R$ with $E_{\rm exc}$. Their explanation relied on the predominance of a selective exciton-formation process assisted by emission of optical phonons (LO), and a faster exciton relaxation due to the increased efficiency of AC-phonon scattering in thinner wells.

From a theoretical point of view, a microscopic approach is needed that is able to treat both free carriers and excitons and their mutual coupling on the same level. To this end, we have extended the conventional kinetic picture in terms of Boltzmann equations for free electrons and holes by a similar equation for bound $1s$ excitons to that in Ref. 10 for bulk systems. The resulting set of kinetic equations has been solved by means of an ensemble Monte Carlo (MC) technique. The MC method is known to be the ideal approach for a realistic description of nonequilibrium carrier dynamics in photoexcited semiconductors[1,9] and, therefore, particularly well suited for such an investigation. In order to clarify the problem of exciton formation and relaxation in quantum wells, we applied this general scheme to quasi-two-dimensional systems, and performed MC simulations of the relaxation dynamics of coupled free-carrier and exciton populations in QW's. In addition to the usual electron and hole scattering mechanisms (carrier-phonon and carrier-carrier interactions), particle interchange between the free-carrier and exciton populations is introduced via formation and dissociation processes which have to be assisted by some partner particle due to energy and momentum conservation.[11] At low densities, the case we are interested in here, phonon-mediated transitions will dominate.

The most prominent effect of the additional spatial confinement in QW structures on exciton states is to increase the binding energy $E_0$ and to shrink the corresponding Bohr radius $a_0$ compared to the bulk values. To describe these modifications, we adopt the fractional dimension approach of Ref. 12 which provides a simple interpolation scheme for $E_0$ and $a_0$ using the known confined single-particle wave functions of electrons and holes.[13]

Figure 1 shows the integrated transition probability for the formation of $1s$ excitons under the emission of one LO phonon in a $GaAs/Al_{0.3}Ga_{0.7}As$ QW with $d = 80$ Å (b) compared to the bulk one (a). The sharp peaks just above the emission thresholds for electrons and holes and their rapid suppression at higher carrier energies are mainly due to the polar character of the Fröhlich interaction as well as to the localization of the excitonic wavefunction in $\mathbf{k}$ space. Their asymmetry comes from the different contributions of electrons and holes to the total exciton polarizability, which is related to the different effective masses. This corresponds to an enhanced formation probability whenever the electron or the hole energy is close to zero. The fact suggests the possi-

 

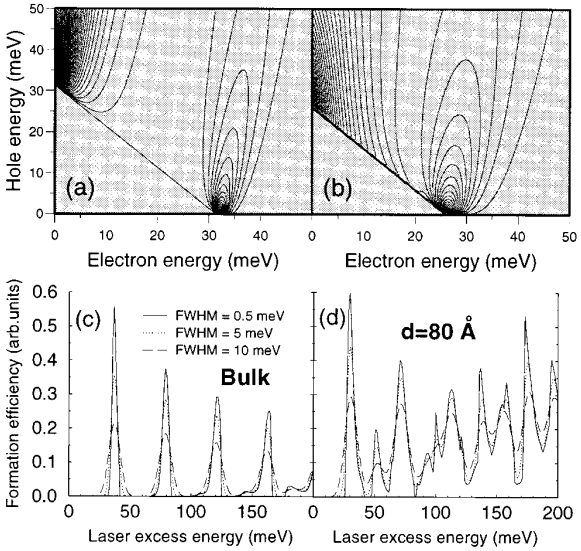


FIG. 1. Contour plots of the integrated transition probability for exciton formation under emission of one LO phonon as a function of $e$ and $h$ energies and the relative formation efficiency vs $E_{\mathrm{exc}}$ (bottom). The three curves correspond to different widths of carrier distribution functions (see text). (a) and (c) bulk GaAs (b) and (d) $GaAs/Al_{0.3}Ga_{0.7}As$ QW with $d=80$ Å.

bility of tuning the laser energy in order to create ''spots'' of free carriers in energy regions where the formation probability is enhanced or not. Assuming that carrier-carrier interaction is not strong enough to suppress the optical-phonon replica in the carrier distribution, one would expect a variation of the rate of exciton formation with the excitation condition. This is true at least during the few picoseconds after photoexcitation, when the carrier distribution is still under nonequilibrium conditions. At the bottom of Fig. 1 we show how the initial formation efficiency depends on the laser excess energy. The value corresponds to an average of the formation probability around the ''spot'' in the $E_e$-$E_h$ plane where the photoexcitation peak or its phonon replica are initially localized. The three curves are calculated starting from Gaussian carrier distributions of different widths. In the following, we will talk about excitation in high (HFE) or low (LFE) formation efficiency regions, respectively, when the photoexcited free-carrier distributions or their phonon replica populate or not regions with enhanced formation probability.

In QW's [Fig. 1(b)], the reduction of the exciton Bohr radius is equivalent to a larger spread of the wave function in **k** space compared to the bulk case. The peaks in the formation probability are less sharp, and the energy range corresponding to LFE conditions is reduced. Furthermore, if we consider the possibility of also exciting carriers from the light-hole subband and assume a ratio of 3:1 for the heavy- and light-hole oscillator strengths, we obtain a more complex dependence of the formation efficiency on laser excess energy [Fig. 1(d)].

While the transitions mediated by LO-phonon interaction show a well-structured dependence on carrier energies, this is not the case for AC-phonon-assisted exciton formation. To discern the two contributions to the formation dynamics, and to elucidate how different conditions can influence the experimental results, we performed several simulated experiments for various physical conditions. In Fig. 2 we show the time evolution of the total densities of free carriers and excitons for two different laser excitations corresponding to HFE and LFE conditions ($E_{\mathrm{exc}}=30$ meV and $E_{\mathrm{exc}}=45$ meV, respectively) in a $GaAs/Al_{0.3}Ga_{0.7}As$ QW with $d=80$ Å. The initial carrier density is $n_{\mathrm{inj}}=1\times10^{10}$ cm$^{-2}$, and the lattice temperature is $T=10$ K. The dynamics of the formation process is characterized by two different temporal regimes. For times shorter than 10–20 ps, we see a fast variation of the carrier density, and the formation rate is quite different for the two excitation conditions reported in the figure. At longer times, on the contrary, the evolution is slower and the differences are less significant.

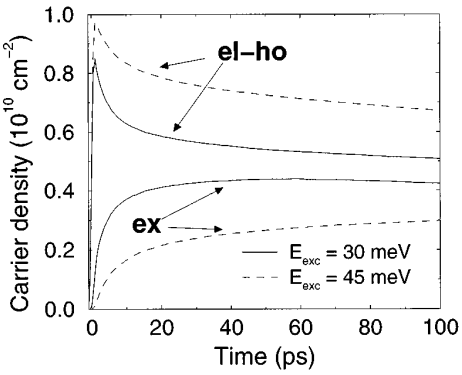


FIG. 2. Free-carrier and exciton densities vs time for two different laser excess energies.

A simplified description of carrier dynamics in terms of the rate equation for carrier populations assumes a bimolecular formation coefficient $C_0$ which is time independent:

$$\left.\frac{dn_x}{dt}\right|_{\mathrm{form}} = -\frac{dn_e}{dt} = C_0 n_e^2(t). \tag{1}$$

However, the different evolution on short- and long-time scales can be actually described only in terms of a time-dependent formation coefficient $C(t)$, which represents the total formation rate due to both LO- and AC-phonon contributions. The probability of the AC-phonon-mediated formation process does not show any particular dependence on free-carrier energies. It is then reasonable to suppose that its contribution does not change with time. Conversely, the LO-phonon mechanism exhibits a minimum threshold for the total energy of the electron-hole pair and, therefore, as far as the carrier plasma cools, the formation rate decreases.

In Fig. 3 we show the separate LO and AC contributions to the total formation coefficient $C(t)$ for the two previous simulation conditions. While the AC-phonon effect is almost time independent, the LO-phonon one has a strong time dependence. Because of that, it is reasonable to rewrite Eq. (1) as

$$\left.\frac{dn_x}{dt}\right|_{\mathrm{form}} = -\frac{dn_e}{dt} = [C_{\mathrm{LO}} e^{-t/\tau_D} + C_{\mathrm{AC}}] n_e^2(t), \tag{2}$$

with $C_{\mathrm{LO}}$ describing the initial LO-phonon formation efficiency, and $\tau_D$ accounting for its roughly exponential decay

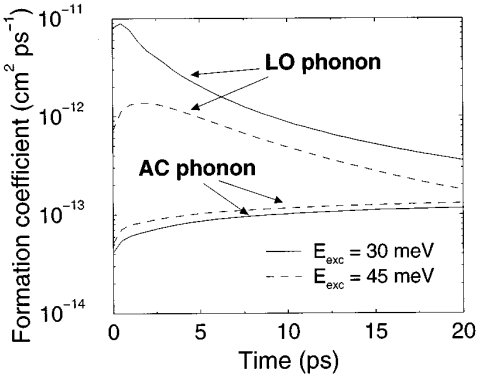


FIG. 3. Time dependence of the bimolecular formation coefficient of LO- and AC-phonon-assisted processes for two different laser excess energies.

due to free-carrier cooling; $C_{\mathrm{AC}}$ gives the constant AC-phonon contribution. Although restricted to short times, the most important contribution to exciton formation is the LO-phonon-mediated mechanism, which acts in a different way for the two distinct excitation conditions.

To quantify such a dependence on the laser excess energy, we performed various simulations tuning $E_{\mathrm{exc}}$ from 20 to 150 meV. From the time evolution of the populations we have extracted the three parameters in Eq. (2). Figure 4 shows $C_{\mathrm{LO}}$ and $\tau_D$ as functions of $E_{\mathrm{exc}}$. No significant dependencies on laser excess energy and carrier density have been found for $C_{\mathrm{AC}}$, whose value is always around $1\times10^{-13}$ cm$^2$ ps$^{-1}$. The oscillatory behavior of $C_{\mathrm{LO}}$ reflects the formation efficiency for the same QW [Fig. 1(d)], thus confirming that a large fraction of excitons is created during the first ps when carriers are not yet thermalized. The value

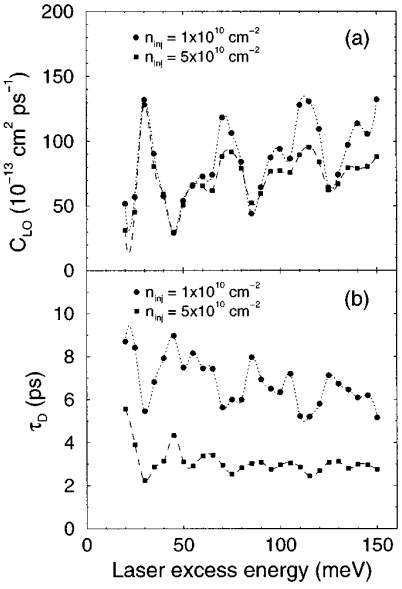


FIG. 4. Laser excess energy dependence of (a) $C_{\mathrm{LO}}$ and (b) $\tau_D$ for different photoexcited carrier densities.

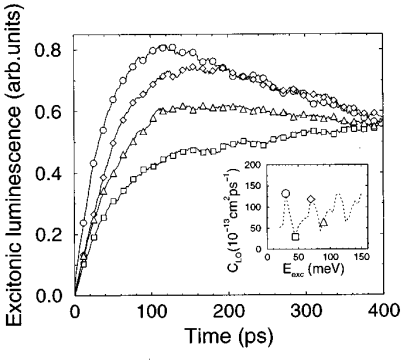


FIG. 5. Temporal evolution of excitonic luminescence for different laser excess energies. Symbols corresponding to different curves, shown in the inset, prove the opposite excitation conditions.

of $\tau_D$ is essentially related to the electron and hole energy relaxation rates: a maximum in the formation coefficient $C_{\mathrm{LO}}$ corresponds to a faster energy loss,[14] and therefore to a lower value of $\tau_D$. Thus $\tau_D$ is smaller when the carrier density is larger and the exciton formation rate—proportional to $n_e^2$—is higher.

Except for one experimental study where the authors extracted information on the intrinsic formation process from free-carrier luminescence,[7] time-dependent exciton formation is usually obtained from indirect measurements of the excitonic luminescence. Unfortunately, the luminescence signal results from of a two-step process: a formation of excitons with relatively large in-plane wave vectors and their subsequent energy relaxation toward the minimum of the excitonic band.

So far, we focused only on the intrinsic formation mechanism. Clearly, in order to compare our simulated experiments with luminescence measurements, we also have to consider the energy relaxation of excitons following their formation. In Fig. 5 we report the luminescence intensity, i.e., the number of excitons having energy within an assumed linewidth of 0.1 meV, as a function of time for the 80-Å QW.

The various curves in the figure correspond to different excess energies corresponding to high or low initial formation efficiency (see the inset). The evident differences between opposite formation-efficiency conditions are mainly consequences of a fast or slow exciton formation, but also depend on the mean energy of the formed excitons. In fact, for HFE excitation most excitons are created very rapidly, with a well-defined kinetic energy of about 2–3 meV, because the carrier distributions are still well localized around the excitation ''spot.'' Conversely, for LFE excitations, LO-phonon emission creates much fewer excitons during the first stage: the relative contribution of AC-phonon formation, giving larger kinetic energies of the order of $E_0\approx10$ meV, is stronger then. This is essentially reflected by the excitonic luminescence, whose time dependence is not simply exponential, as can be seen in Fig. 5.

In the relatively wide QW's considered here, the energy relaxation due to AC-phonon scattering is comparably slow, and the rise times $\tau_R$ of the luminescence are quite long. This means that the relative effect of the excitation conditions

might be somewhat obscured. In narrower QW's the energy relaxation of excitons would be faster due to enhanced AC-phonon scattering,[5] and the time evolution of the total exciton density would be reflected more directly by $\tau_R$. One would expect clearer indications of the excess-energy dependence of the formation rate in the rise time of luminescence there. However, in this Rapid Communication the LO phonons have been described as dispersionless GaAs bulk modes, which is reasonable for QW's of 80 Å. For decreasing well widths a more realistic phonon model is needed to describe the variety of confined and interface modes[15,16] with different energies and interaction strength. As an example, in a 26-Å QW like the sample of Blom *et al.*,[5] the scattering rate related to the (barrier) AlAs-like phonon modes is comparable to that of the GaAs-like ones.[16] We do not aim to model this situation. However, although we believe that the main results of the present study will remain qualitatively correct for narrow wells, we would expect a modified dependency on the excess laser energy that could not be related to the GaAs LO-phonon energy alone.

In summary, we have shown that the exciton-formation process in QW's at low carrier densities is mainly due to LO-phonon emission during the first few ps after photoexcitation. At longer times the importance of this mechanism reduces exponentially, so that finally only AC-phonon-mediated formation survives. Since the fast LO-phonon-related binding is highly selective in energy, free carriers can be excited such to give either fast or slow exciton binding. Compared to bulk systems,[10] this general behavior is modified in QW's due to a less structured formation probability and due to the presence of several subbands. There are, however, always two distinct temporal regimes related to the two different phonon-assisted binding channels. The analysis of the temporal evolution of excitonic luminescence additionally has to take into account the exciton energy relaxation process which, in turn, cannot be seen as independent from the actual excitation conditions and the time elapsed after the laser pulse.

[1] See, e.g., J. Shah, *Ultrafast Spectroscopy of Semiconductors and Semiconductor Nanostructures* (Springer, Berlin, 1996), and references therein.

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[9] See, e.g., S. M. Goodnick and P. Lugli, in *Hot Carriers in Semiconductor Nanostructures: Physics and Applications*, edited by J. Shah (Academic, San Diego, 1992), p. 191 and references therein.

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[13] The values obtained for the heavy-hole exciton in a GaAs/$Al_{0.3}Ga_{0.7}As$ QW of 80-Å width are $E_0 = 10.2$ meV and $a_0 = 71$ Å. They are evaluated using a heavy-hole effective mass $m_{hh} = 0.52 m_0$, obtained from an interpolation of the nonparabolic valence-band dispersion.

[14] In addition to the other energy-relaxation mechanisms, exciton formation processes via emission of LO phonons also cool the electron-hole plasma, since the total energy of the particles forming the exciton is larger than the mean free-carrier energy.

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